

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-01881a. REPORT SECURITY CLASSIFICATION
UNCLASSIFIED

1b. RESTRICTIVE MARKINGS

AD-A218 552

EB 27 1990

3. DISTRIBUTION/AVAILABILITY OF REPORT

Approved for public release;
distribution is unlimited.

(2)

5. MONITORING ORGANIZATION REPORT NUMBER(S)

AFOSR-TR- 90-0189

6a. NAME OF PERFORMING ORGANIZATION
MIT6b. OFFICE SYMBOL
(If applicable)7a. NAME OF MONITORING ORGANIZATION
AFOSR/NC

6c. ADDRESS (City, State, and ZIP Code)

Cambridge, MA 02139

7b. ADDRESS (City, State, and ZIP Code)

Building 410, Bolling AFB DC
20332-64488a. NAME OF FUNDING SPONSORING
ORGANIZATION

AFOSR

8b. OFFICE SYMBOL
(If applicable)

NC

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

F49620-86-C-0003

8c. ADDRESS (City, State, and ZIP Code)

Building 410, Bolling AFB DC
20332-6448

10. SOURCE OF FUNDING NUMBERS

PROGRAM
ELEMENT NO.

61102F

PROJECT
NO.

2303

TASK
NO.

B1

WORK UNIT
ACCESSION NO.

11. TITLE (Include Security Classification)

(U) REACTIONS OF LASER-GENERATED FREE RADICALS AT SEMICONDUCTOR SURFACES.

12. PERSONAL AUTHOR(S)

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13a. TYPE OF REPORT

Final

13b. TIME COVERED

FROM 10/1/85 TO 12/31/89

14. DATE OF REPORT (Year, Month, Day)

22 January 1990

15. PAGE COUNT

6

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD

GROUP

SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

surface chemistry,

fluorocarbon chemistry,

laser photochemistry,

silicon hydrides.

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Reactions of laser-generated free radicals at semiconductor surfaces have been investigated by photoelectron spectroscopy of adsorbed surface layers and by laser-induced fluorescence detection of the gas-phase species. Systems investigated include dissociative chemisorption of XeF_2 and CF_3 on $\text{Si}(111)$, IR multiple-photon dissociation of alkylsilanes and characterization of the SiH_2 dissociation product and deposition of metallic films from iron carbonyl. From these experiments, quantitative models have been developed for the reactivity of fluorocarbon radicals at silicon surfaces, intersystem state coupling in excited SiH_2 , and formation of metallic films.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT

☒ UNCLASSIFIED/UNLIMITED☒ SAME AS RPT☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION

UNCLASSIFIED

22a. NAME OF RESPONSIBLE INDIVIDUAL

L P DAVIS, MAJOR, USAF

22b. TELEPHONE (Include Area Code)

(202) 767-4963

22c. OFFICE SYMBOL

AFOSR/NC

FINAL REPORT

to the

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

on

Contract F49620-86-C-0003

"Reactions of Laser-Generated Free Radicals
at Semiconductor Surfaces"

by

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(22 January 1990)

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Introduction

The reactions of neutral fluorocarbon free radicals at silicon-containing surfaces are an important component of the mechanism of reactive etching of such surfaces during the production of microelectronic devices; however, isolating such reactions in a plasma environment is difficult or impossible, because of the simultaneous presence of other reactive species such as energetic ions and electrons. For this reason, we have used photolytic methods for selective generation of such radicals and subsequent investigation of their reactions with semiconductor surfaces, such as silicon and silicon oxides.

Reactions of Laser-Generated Fluorocarbon Radicals at Silicon-containing Surfaces.

The radicals CF_3 and CF_2 have been produced by infrared multiphoton dissociation (IRMPD) or u.v. photodissociation, respectively, of perfluorinated precursor species, and the overlayers resulting from reaction of these radicals with adjacent silicon-containing surfaces have been examined by X-ray Photoelectron Spectroscopy, Auger Electron Spectroscopy, and Thermal Desorption Spectrometry [11, 15, 16, and 17]*. On the basis of these results, and complementary experiments using molecular fluorinating agents such as XeF_2 [4, 10] and NF_3 [18,19], we have proposed a simple theoretical model based on the strengths of chemical bonds made and broken at the reacting surface, which appears to account satisfactorily for most of the observed behavior [16,18]. The CF_3 radical can bind to dangling bonds on the $\text{Si}(111)$ or $\text{Si}(100)$ surface, but does not do so readily on the SiO_2 surface because breaking the surface Si-O bond requires more energy than is returned by forming a Si-C bond. The SiO_2 surface must first be disrupted e.g., by argon-ion bombardment, to create binding sites for CF_3 . On a Si surface, a bound CF_3 will transfer at least some of its fluorine atoms because of the greater binding energy of Si-F vs. C-F. On a SiO_2 surface, such transfer is inhibited because both a C-F and a Si-O bond must be broken in order to produce the Si-F bond. CF_2 appears to bind more readily to SiO_2 than does CF_3 ; this can be understood on the basis of the divalent carbon producing a new Si-C and a C-O bond, which compensates for the energy required in the Si-O bond breaking step. In the case of valence-saturated species, such as XeF_2 on SiO_2 , there appears to be a substantial barrier to dissociative chemisorption.

Related experiments were also carried out to characterize the IRMPD process utilized for production of CF_3 radicals [3, 5], and the product-state distribution and surface loss coefficient of CF_2 radicals produced by u.v. photodissociation of C_2F_4 [6, 21].

* Numbers in brackets refer to the list of publications which follows.

Laser-Initiated Chemical Vapor Deposition

Laser-initiated dissociation of gas-phase precursors can also lead to deposition of thin films, e.g. of amorphous silicon [7, 20] or metallic materials. In the IRMPD of organosilanes and silicon hydrides, silylene has been postulated as a key intermediate leading to deposition of silicon films. The SiH₂ fragment so produced has been detected by laser-induced fluorescence (LIF) [1]. A remarkable variation in the fluorescence lifetimes of individual rovibronic levels of the \tilde{A}^1B_1 state of SiH₂ is observed, with decay rates varying by over two orders of magnitude between neighboring transitions [8]. This variation is attributed to mixing of the \tilde{A} state with high vibrational levels of the \tilde{X}^1A_1 state and/or nearby triplet states, such as the \tilde{a}^3B_1 or the 3A_2 , and with the dissociative continuum of Si(³P)+H₂. The distribution of lifetimes has been examined from an information-theoretic point of view, in collaboration with Professor R.D. Levine and his co-workers at the Hebrew University [9, 14]. The measured distribution is well fitted by a maximal-entropy expression for the decay rates, which in turn implies that the level spacings distribution at ca. 18,000 cm⁻¹ total energy in the neighboring triplet and \tilde{X}^1A states is chaotic and uniformly samples its available phase space.

By extending the LIF measurements to higher vibrational levels in the (0v₂0) manifold, including the region at which calculations by Francisco and co-workers indicate that the Si(¹D₂) dissociation channel becomes available [12], we are able to establish the location of the Si(¹D₂) + H₂ dissociation channel. Its position, between v₂'=6 and 7, allows us to determine the standard heat of formation of SiH₂(g) as $\Delta H_f^\circ = (65.4 \pm 1.6) \text{ kcal mole}^{-1}$. [13].

Experiments have also been undertaken to characterize the processes occurring in deposition of metallic films from u.v. photolysis of metal carbonyls such as Fe(CO)₅. From XPS and Auger analysis of the deposited films, and measurements of their growth rate, we have developed a model which includes both gas-phase initiation and subsequent dissociation (thermally and/or photochemically driven) of the photodeposited material [22].

Although a satisfying portion of the work originally proposed was accomplished during this research program, with a number of significant findings reported in the process, there still remain many further important unresolved questions concerning the dynamics of laser-initiated gas-surface reactions. It is clear, for example, that the thermochemical model developed for radical-surface reactions [16] cannot account satisfactorily for reactions in which there is a substantial energy barrier in the dissociative chemisorption channel. More accurate *ab initio* or semi-empirical models of adsorbate-surface interaction energies are now beginning to appear, and should be applied to the systems we have studied. There are also intriguing suggestions, both in our work [6, 20] and results from other laboratories, that the reactivity of radicals at surfaces depends strongly on their vibrational energy content. State-resolved optical

diagnostics, such as LIF and REMPI, afford the possibility of investigating such dependences. Finally, our results on photodeposition of metallic films from carbonyls [22] suggests the possibility of photodissociation processes occurring in the freshly deposited materials which differ substantially from analogous gas-phase processes. All of these questions have interesting implications for molecular dynamics, as well as addressing practical issues of improved efficiency and control for photon-driven processes in microelectronic device fabrication. It is thus regrettable that this research program has not been continued.

Accession for	
NTIS - Obit	<input checked="" type="checkbox"/>
DTIC - Tech	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution /	
Approved	
Date	
A-1	



Cumulative List of Publications (10/1/85 - 12/31/89)

- *1. J.W. Thoman, Jr. and J.I. Steinfeld, "Laser Excited Fluorescence Detection of SiH₂ Produced in IRMPD of Organosilanes," Chem. Phys. Letts. 124, 35 (1986).
- *2. K Suzuki, K. Ninomiya, S. Nishimatsu, J.W. Thoman, Jr., and J.I. Steinfeld, "Analytical Investigation of Plasma and Electrode Potentials in a Diode Type RF Discharge," Japanese J. Appl. Phys. 25, 1569 (1986).
- *3. J.S. Francisco and J.I. Steinfeld, "Photochemistry, Photophysics, and Spectroscopy of Molecular Infrared Multiple Photon Excitation," Advances in Multiphoton Processes and Spectroscopy, Vol. 2 (S.H. Lin, ed.), World Scientific Publishing Pte Ltd., Singapore (1986), pp. 79-173.
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- *8. J.W. Thoman, Jr., J.I. Steinfeld, R.I. McKay, and A.E.W. Knight, "Wide Fluctuations in Fluorescence Lifetimes of Individual Rovibronic Levels in SiH₂(\tilde{A}^1B_1)" J. Chem. Phys. 86, 5909 (1987).
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- *17. J. Langan, J.A. Shorter, Xu Xin, and J.I. Steinfeld, "Reactions of Photogenerated CF_2 and CF_3 on Silicon and Silicon Oxide Surfaces", *Proc. Materials Research Society Fall Meeting* (Boston, Massachusetts, November 1988).
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19. J.A. Shorter, J. Langan, and J.I. Steinfeld, "Reactions of NF_3 at Silicon and Silicon Oxide Surfaces", *Surf. Sci. Lett.* **219**, L560 (1989).
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21. O. Suto and J.I. Steinfeld, "Time-Resolved Diode Laser Absorption Spectroscopy of CF_2 Produced in u.v. photodissociation of C_2F_4 and measurement of the ν_3 absorption band strength," submitted to *Chem. Phys. Letts.*
- *22. Xu Xin and J.I. Steinfeld, "Gas-phase and surface dissociation mechanisms in u.v. laser Photodeposition of iron films from $\text{Fe}(\text{CO})_5$ ", manuscript in preparation.
23. J.I. Steinfeld, "Reactions of Laser-Generated Free Radicals at Semiconductor Surfaces", Final Technical Report.

(* reprint not available)